Evaluation of Reagents for the Chemical Enhancement of Fingermarks on Porous Surfaces: Optimisation and Characterisation of the 1,2-Indanedione Technique

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Certificate of Authorship and Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature are indicated in the thesis.

C Wallace

Christie Wallace - Kunkel

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ACT – Australian Capital Territory

AFP – Australian Federal Police

CFC – Chlorofluorocarbons

CI – Chemical Imaging

CPMAS – Cross Polarization Magic Angle Spinning

DFO – 1,2-diazofluorenone

DIFS – Division of Identification and Forensic Science (Israel Police)

DMSO – Dimethyl sulfoxide

DSC – Differential Scanning Curves

DTG – Derivative Thermogravimetry

ESMS – Electrospray Mass Spectrometry

FBI – Federal Bureau of Investigations

FLS – Forensic Light Source

ENFSI – European Network Of Forensic Science Institutes

HFC 4310mee – 1,1,1,2,3,4,4,5,5,5-decafluoropentane

HFE 7100 – 1-methoxynonafluorobutane

HFE 71de – 1-methoxynonafluorobutane and 1,2-dichloroethylene

HOSDB – Home Office Scientific Development Branch

IAI – International Association for Identification

IFRG – International Fingerprint Research Group

IND – 1,2-Indanedione

INDZN – Formulation of 1,2-Indanedione containing zinc

IR – Infrared

LCTF – Liquid Crystal Tuneable Filter

MS – Mass Spectrometry

NMR – Nuclear Magnetic Resonance

SWGFAST – Scientific Working Group Friction Ridge Analysis, Study and Technology

TGA – Thermogravimetric Analysis

TLC – Thin Layer Chromatography

USSS – United States Secret Service

UTS – University of Technology, Sydney

UV-VIS – Ultraviolet – Visible

VSC 2000 – Video Spectral Comparator 2000

ABSTRACT

There is a continual search for new and improved reagents to detect fingermarks on a variety of surfaces. With increased technology and resources the possibilities are continually expanding. 1,2-Indanedione is a relatively new reagent for the development of fingermarks on porous surfaces. Its boundaries have not been completely explored nor has the method of reaction with fingermarks been determined. The initial aim of this project was to investigate the fingermark reagent 1,2-indanedione and determine if it was a viable reagent for routine use in Australia. The secondary aim was to study the reaction that occurs between 1,2-indanedione and amino acids and the subsequent reaction with metal salts to gain further insight into the reaction than has been previously published. Additionally the fingermark reagent 5-methylthioninhydrin, which although had shown good results in detecting fingermarks in the early 1990's, did not seem to be widely used or studied since its commercial manufacture began. A new reagent for the problematic and increasingly encountered thermal paper, ThermaNin, was also evaluated and compared to other proposed methods for the development of fingermarks on thermal paper.

The investigation of 1,2-indanedione as a fingermark reagent for use in Australia was performed by comparing a number of formulations and development procedures, encompassing all published recommendations as well as some novel approaches. 1,2-indanedione formulations were compared with respect to initial colour, fluorescence, concentration of the reagent, acetic acid concentration and the effect of different carrier solvents.

Numerous development conditions were also investigated, including a conventional oven, a heat press and humidity. Further enhancement using metal salts and liquid nitrogen was also evaluated. The heat press set at 165 ^{0}C for 10 s proved to give the best initial colour and most intense luminescence. Secondary metal salt treatment improved initial colour and luminescence and was found to provide consistent results despite different environmental conditions. It is for this reason that it is recommended that metal salt treatment consistently be performed after treatment with 1,2-indanedione or included in the formulation of 1,2-indanedione. The Polilight, the VSC 2000, and the Condor Chemical Imaging macroscope have been used to detect fingermarks developed with 1,2-indanedione on a variety of high- and low- quality porous and semi-porous surfaces with impressive results overall.

Laboratory and field tests were conducted to compare 1,2-indanedione with DFO and ninhydrin as well as to investigate the position of 1,2-indanedione in the sequence of reagents for fingermark detection on porous surfaces.
Overall 1,2-indanedione proved to be a viable alternative to tradition methods for the detection of fingermarks on porous surfaces, with more fingermarks being developed using this reagent on real samples than both DFO and ninhydrin and a combination of the two reagents.
The isolation of a single pure product from the reaction of 1,2-indanedione with several different amino acids was not achieved. The study was able to establish that 1,2-indanedione reacts differently with different amino acids with some reactions, such as those with alanine and cysteine, following a similar pathway. A study performed by nuclear magnetic resonance spectroscopy and colour reactions showed that increasing the content of water in the reaction retarded the kinetics of the reaction and thus it is possible that the concentration of water in the reaction may influence the path the reaction takes. Solid state nuclear magnetic resonance spectroscopy indicated that the product of the reaction is ionic, which may help explain the problems encountered on separation and isolation of the product. Thermal and elemental analysis provided some information on the by-products released by the reaction, whilst mass spectroscopy provided information on the possible pathway of the reaction.
The results of this study support the proposal made by Petrovskaia (1999) that the main reaction product of 1,2-indanedione and amino acids is a Ruhemann's purple type product with a molecular mass of 275.
A study of the reaction between metal salts and the 1,2-indanedione/amino acid product was also performed on a crude reaction mixture. This was due to the inability to provide a pure starting materials as well as the unsuccessful separation of the complex by thin layer chromatography. The information gained; however, from a study via nuclear magnetic resonance spectroscopy, mass spectroscopy, UV-visible spectroscopy and infrared spectroscopy indicates that two 1,2-indanedione molecules react with the nitrogen atom in the amino acid forming a tridentate ligand which then complexes with the metal ion.
The evaluation of 5-methylthioninhydrin found that the reagent is superior to ninhydrin; however, 1,2-indanedione exhibits much stronger luminescence when used to treat latent

fingermarks. The high cost of the reagent accompanied by the fact that 1,2-indanedione was found to be a superior reagent and is already in use in many laboratories precludes a recommendation for its routine use.

ThermaNin was evaluated against other recommended reagents for the development of fingermarks on thermal paper. ThermaNin itself was found to be extremely sensitive to water and humidity and must be made fresh before its use due to poor stability. Once again a 1,2-indanedione formulation, albeit without acetic acid, was found to be the optimal method to detect fingermarks on this particular surface.

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Forewards

CHAPTER 1 – Introduction

Chapter 1 presents an introduction to fingermarks including history, identification, enhancement and detection. It includes an introduction to the reagents used to detect and enhance fingermarks on porous surfaces focusing on ninhydrin, DFO, 1,2-indanedione, 5-methylthioninhydrin and Thermanin, and the pervious research conducted into these reagents. A brief outline of the aims of this research is also reported.

CHAPTER 2 – Fingermarks on Porous Surfaces – A Survey

Chapter 2 present a survey which was conducted into the types, formulations and frequency of reagents used to develop fingermark son porous surfaces with the specific aim of gathering information on the awareness, opinion and level of use of the fingermark reagent 1,2-indanedione. The results of the survey are reported and discussed.

Wallace-Kunkel, C., Roux, C., Lennard, C. & Stoilovic, M. (2004) The Detection and Enhancement of Latent Fingermarks on Porous Surfaces - A Survey *Journal of Forensic Identification* 54(6): 687-705

CHAPTER 3 – Optimisation of 1,2-Indanedione

Chapter 3 focused on the investigation of all recommended formulations, development and detection conditions of fingermark treated with 1,2-indanedione. It presents the optimum conditions for the use of the reagent under Australian conditions. Eight formulations in total were investigated as well as novel formulations, the effect of a heat press, a standard oven and added humidity were determined as well as the use of metal salt treatment and cooling with liquid nitrogen. The Polilight, the VSV 2000 and the Condor Chemical Imaging system were all investigated as methods of detection.

Wallace-Kunkel, C., Lennard, C., Stoilovic, M. & Roux, C. (2007) Optimisation and Evaluation of 1,2-Indanedione for use as a Fingermark Reagent and its Application to Real Samples *Forensic Science International* 168: 14-26 **Awarded National Institute of Forensic Science (NIFS) Best Technical Article for 2007**

CHAPTER 4 – Applications of 1,2-Indanedione

In Chapter 4 the formulation of 1,2-indanedione optimised in Chapter 3 is compared with ninhydrin and DFO through the sensitivity of detection of the reagents using amino acids, test samples and through real and randomly laid samples. The position of 1,2-indanedione in the sequence of reagents for the development of fingermarks on porous surfaces was determined as well as the performance of 1,2-indanedione on difficult porous and semi porous surfaces. A further investigation into the effect of environmental conditions and the effect zinc metal salt is also reported.

Stoilovic, M., Lennard, C., Wallace-Kunkel, C. & Roux, C. (2007) Evaluation of a 1,2-Indanedione Formulation Containing Zinc Chloride for Improved Fingermark Detection on Paper *Journal of Forensic Identification* 57(1): 4-18

CHAPTER 5 – A Study of the 1,2-Indanedione/ Amino Acid Reaction

Chapter 5 reports experiments which aim to gain more insight into the reaction of 1,2-indanedione with amino acids using various instrumental methods including TLC, UV-Vis, IR, NMR, MS, elemental analysis and thermal analysis. A preliminary study into the secondary reaction including metal salts, which had not been previously studied, is also investigated using similar instrumental means.

CHAPTER 6 – Other Reagents for Fingermarks on Porous Surfaces

Chapter 6 presents other applications of 1,2-indanedione as well as investigations into other amino acid specific reagents, 5-methylthioninhydrin and thermanin. 5-Methylthioninhydrin and ThermaNin are two reagents that have been commercially manufactured without a full evaluation of optimum formulation either before manufacture or after. 5-Methyltioninhydrin was evaluated by means of a carrier solvent study, a spectroscopy study, comparison with the conventional reagents, ninhydrin and DFO, and a price comparison.

Thermal paper has often proved problematic for fingermark development. ThermaNin has been recently proposed as a reagent for use on thermal paper. The formulation of ThermaNin was optimised and compared against other proposed reagents for fingermark development on thermal paper such as 1,2-indanedione, 'Nin-dry' and a ninhydrin formulation for thermal paper. A novel method for development on fingermarks on thermal paper 'Ind-dry' was also proposed and evaluated.

Wallace-Kunkel, C., Lennard, C., Stoilovic, M. & Roux, C. (2006) Evaluation of 5-Methylthioninhydrin for the Detection of Fingermarks on Porous Surfaces and Comparison to Conventional Reagents *Identification Canada* 29(1): 4-13